

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

**DECLARATION**

I, Michele Grange, BA., MITI., translator to Messrs. Taylor and Meyer of 20 Kingsmead Road, London SW2 3JD, England, do solemnly and sincerely declare as follows:

1. That I am well acquainted with the English and German languages;
2. That the following is a true translation made by me into the English language of German Priority Text Application No. 102 58 858.9;
3. That all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true;  
and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardise the validity of the application or any patent issued thereon.

Signed, this 4<sup>th</sup> day of April 2008

M. Grange

**Pyrogenically produced silica**

The invention provides a pyrogenically produced silica powder, the production thereof and its use.

- The term fumed silica or pyrogenic silica covers all highly disperse silicas which are obtained in the gas phase at high temperatures by coagulation of monomeric silica. There are two processes for the technical production of pyrogenic silicas: high-temperature hydrolysis and the electric-arc process.
- In the high-temperature hydrolysis process, a homogeneous mixture of a vaporous silicon compound, generally silicon tetrachloride, hydrogen, oxygen and an inert gas is burnt with a burner in a cooled combustion chamber. During this process, the following reactions take place simultaneously:
1.  $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$       2.  $\text{SiCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{HCl}$

Because of the homogeneity of the gas mixture, the reaction conditions and thus the conditions for the formation and growth of each  $\text{SiO}_2$  particle are largely identical, so that very uniform and even particles can form. In the known process, air is used as the source of oxygen. The pyrogenic silicas produced by the known process have specific surfaces of between 10 and 600  $\text{m}^2/\text{g}$ .

EP-A-759410 describes the production of a pyrogenic silica powder with a surface area of less than 90  $\text{m}^2/\text{g}$ , preferably less than 60  $\text{m}^2/\text{g}$ , and a dibutyl phthalate number (DBP number), expressed as g of dibutyl phthalate/100 g of silica powder, of less than 60. The DBP number is a measure of the structure or the degree of fusion of the particles of the powder. A low structure is expressed by a low DBP number. The silica powder described in EP-A-759410 accordingly exhibits a comparatively low structure with a comparatively low surface area. An essential feature of the process for the production of the powder is the preheating

of the mixture of silicon compound and air to temperatures of approx. 400 degrees Celsius.

The combination of low surface area and low structure is explained further in EP-A-1182168. Dispersions of the 5 silica powder produced there have particularly low viscosity. The basic silica powder has little structuring.

The prior art describes silica powder with a low surface area and with a low structure. However, it is not possible to produce a silica powder by the processes described in 10 EP-A-759410 and EP-A-1182168, for example, which has a similarly low surface area but is clearly more strongly structured. A material like this could, for example, be used where a high thickening action is desirable with a low surface area.

15 The object of the invention thus consists in providing a silica powder which is highly structured compared with the prior art, with a low BET surface.

The invention provides a pyrogenically produced silica powder, which is characterised in that it has

- 20 . . .  
- a BET surface of 30 to 90 m<sup>2</sup>/g,  
- a DBP number of at least 80, expressed as  
g of dibutyl phthalate/100 g of silica and  
- a tamped density of no more than 110 g/l.

The BET surface can preferably be between 35 and 75 m<sup>2</sup>/g, 25 and particularly preferably between 40 and 60 m<sup>2</sup>/g. The BET surface is determined in accordance with DIN 66131.

The DBP number can preferably be greater than 100 and particularly preferably greater than 110. For the DBP absorption, the force uptake, or the torque (in Nm), of the 30 rotating blades of the DBP measuring instrument is measured on addition of defined quantities of DBP, comparable to a titration. A sharply defined maximum is obtained for the powder according to the invention, with a subsequent drop at a specific addition of DBP.

The tamped density is determined on the basis of DIN ISO 787/XI K 5101/18 (not sieved). The tamped density can be altered by further process steps, such as bagging or rolling. In the powder according to the invention,  
5 regardless of this, it is less than 110 g/l. It can preferably be less than 100 g/l.

In another preferred embodiment, the silica powder according to the invention can have an average aggregate circumference of at least 1000 nm. An average aggregate  
10 circumference of at least 1200 nm is particularly preferred. The aggregate circumference can be determined e.g. by image analysis of the TEM images. Aggregate, within the meaning of the invention, refers to primary particles of similar structure and size which have fused together,  
15 the surface area of which is smaller than the sum of the individual, isolated primary particles. The term primary particles, within the meaning of the invention, refers to particles that are initially formed in the reaction and can coalesce as the reaction progresses to form aggregates.  
20 In addition, the kurtosis (steepness), which is a measure of the type of distribution at the edges, of the aggregate area of the powder according to the invention can be at least 20 according to ASTM 3849-89.

The silica powder according to the invention can have a pH  
25 value, measured in a 4% aqueous dispersion, of between 3.8 and 5.

The invention also provides a process, which is characterised in that at least one vaporous silicon compound, a gas containing free oxygen and a combustible  
30 gas are mixed together in a closed burner and then burnt in a flame in the flame tube of the burner, the solid obtained is separated from the gas mixture and optionally purified, wherein

- the oxygen content of the gas containing free oxygen is adjusted such that the lambda value is greater than or equal to 1, and
  - the gamma value is between 1.2 and 1.8.
- 5 Adjustment to a gamma value of 1.4 to 1.6 can preferably be made.
- In the closed burner method, the reaction mixture burns in a flame tube closed to the atmosphere. By comparison, in the open method the reaction mixture would burn in a flame  
10 tube open to the atmosphere.
- As silicon-containing compounds, silicon halides, organochlorosilicon compounds or organosilicon compounds and mixtures of the above compounds can preferably be used. Silicon tetrachloride, methyltrichlorosilane or  
15 tetramethoxysilane can particularly preferably be used.

The invention also provides the use of the silica powder according to the invention for toner applications, in the silicone and rubber industry, to adjust the rheology of liquid systems, for the production of dispersions, as a  
20 filler, for the film-coating of polyethylene terephthalate and polyvinyl acetate, in lacquers and paints.

#### Examples

The dibutyl phthalate absorption is measured with a  
25 RHEOCORD 90 instrument from Haake, Karlsruhe. For this purpose, 12 g of the silica powder, to an accuracy of 0.001 g, are charged into a kneading chamber, this is sealed with a lid and dibutyl phthalate is metered in through an aperture in the lid at a preset metering rate of  
30 0.0667 ml/s. The kneader is operated at a motor speed of 125 revolutions per minute. After reaching the maximum torque, the kneader and the DBP metering are automatically switched off. The DBP absorption is calculated from the quantity of DBP consumed and the quantity of the particles  
35 weighed in according to the following:

DBP number (g/100 g) = (DBP consumption in g / quantity of powder weighed in, in g) x 100.

The pH is determined on the basis of DIN ISO 787/IX, ASTM D 1280, JIS K 5101/24.

- 5 The image analyses are performed using a TEM instrument from Hitachi H 7500 and a MegaView II CCD camera from SIS. The image enlargement for the evaluation was 30000 : 1 with a pixel density of 3.2 nm. The number of particles evaluated was greater than 1000. Preparation took place in  
10 accordance with ASTM 3849-89. The lower threshold limit with respect to detection was 50 pixels.

Lambda is the ratio of supplied oxygen in the core to stoichiometrically required oxygen.

- Gamma is the ratio of supplied hydrogen in the core to  
15 stoichiometrically required hydrogen.

**Example 1 (comparative example):**

- 500 kg/h of SiCl<sub>4</sub> are evaporated at approx. 90°C and transferred into the central tube of an open burner of  
20 known design. In addition, 145 Nm<sup>3</sup>/h of hydrogen and 207 Nm<sup>3</sup>/h of air with an oxygen proportion of 35 vol.% are fed into this tube. This gas mixture is ignited and burns in the flame tube of the water-cooled burner. An additional 15 Nm<sup>3</sup>/h of hydrogen are fed into an outer nozzle  
25 surrounding the central nozzle, to avoid any caking. An additional 250 Nm<sup>3</sup>/h of air of normal composition are fed into the flame tube. After the reaction gases have cooled, the pyrogenic silica powder is separated from the gases containing hydrochloric acid in using a filter and/or a  
30 cyclone. In a deacidification unit, the pyrogenic silica powder is treated with water vapour and air.

**Example 2 (embodiment example):**

500 kg/h of SiCl<sub>4</sub> are evaporated at approx. 90°C and transferred into the central tube of a closed burner of known design. An additional 160 Nm<sup>3</sup>/h of hydrogen and 5 238 Nm<sup>3</sup>/h of air with an oxygen proportion of 34 vol.% are fed into this tube. This gas mixture is ignited and burns in the flame tube of the water-cooled burner. In addition, 15 Nm<sup>3</sup>/h of hydrogen are fed into an outer nozzle surrounding the central nozzle, to avoid any caking. An 10 additional 250 Nm<sup>3</sup>/h of air of normal composition are fed into the flame tube.

After the reaction gases have cooled, the pyrogenic silica powder is separated from the gases containing hydrochloric acid using a filter and/or a cyclone. In a deacidification 15 unit, the pyrogenic silica powder is treated with water vapour and air.

The powders 3 to 5 are produced as in example 2. The experimental conditions are given in Table 1. The analytical data of the powders 1 to 5 are given in Table 2.  
20 **Table 1: Experimental conditions and flame parameters calculated therefrom**

Example		1	2	3	4	5
SiCl <sub>4</sub>	kg/h	500	500	500	500	500
H <sub>2</sub> core	Nm <sup>3</sup> /h	145	160	190	210	240
Air	Nm <sup>3</sup> /h	207	238	326	371	405
H <sub>2</sub> mantle	Nm <sup>3</sup> /h	15	15	15	15	15
lambda		1.1	1.0	1.0	1.0	1.0
gamma		1.0	1.2	1.4	1.6	1.8

Table 2: Analytical data of the silica powders 1-5

Example		1	2	3	4	5
BET	m <sup>2</sup> /g	46	43	46	50	46
DBP	g/100g	76	91	96	107	127
Tamped density <sup>(\\$)</sup>	g/l	53	38	33	28	25
pH <sup>(#)</sup>		4.5	4.5	4.7	4.7	4.8

\\$) direct from the process after purification step; #) 4 wt.-% disp.

Table 3: Aggregate structure of the silica powders of  
5 Examples 1, 3 and 4 by image analysis.

Ex- ample	av. area	av. circum- ference	ø <sup>(*)</sup> max	ø min	Elong- ation	Kurtosis area	SF <sup>(#)</sup>
	nm <sup>2</sup>	nm	nm	nm	nm		
1	23217	1032	292	207	1.78	14.41	39.1
3 <sup>(\\$)</sup>	32780	1475	303	186	2.02	27.27	88.7
4 <sup>(\\$)</sup>	29577	1447	293	179	2.01	25.38	101.1
3 <sup>(&amp;)</sup>	26217	1313	279	141	2.01	21.49	82.9
4 <sup>(&amp;)</sup>	24527	1257	259	161	2.00	24.76	97.1

\*) ø = Diameter; #) Sphericity Factor acc. to ASTM; \\$) Powder before compacting; &) Powder after compacting

- Figure 1 shows a circumference distribution of aggregates.  
10 It shows the relative frequency (in %) with which a certain range of the aggregate diameter (in nm) occurs in the powder. The x-axis should be read here as: up to 1000 nm, up to 1001 to 2000 nm, 2001 to 3000 nm etc.

- A refers to the distribution of the aggregate circumference of a powder not according to the invention with a BET surface of approx. 50 m<sup>2</sup>/g. B shows the distribution of the

aggregate circumference from the powder according to the invention from Example 2. The clearly broader distribution of the aggregates of the powder according to the invention can be seen.

**Claims:**

1. Pyrogenically produced silica powder characterised in that it has
  - a BET surface of 30 to 90 m<sup>2</sup>/g,
  - a DBP number of at least 80, expressed as g of dibutyl phthalate/100 g of silica and
  - a tamped density of no more than 110 g/l.
2. Silica powder according to claim 1, characterised in that the average aggregate circumference is at least 1000 nm, particularly preferably at least 1200 nm.
3. Silica powder according to claims 1 or 2, characterised in that the kurtosis of the aggregate area is at least 20.
4. Silica powder according to claims 1 to 3, characterised in that it has a pH value, measured in a 4 per cent aqueous dispersion, of between 3.8 and 5.
5. Process for the production of the silica powder according to claims 1 to 4, characterised in that at least one vaporous silicon compound, a gas containing free oxygen and a combustible gas are mixed together in a closed burner and then burnt in a flame in the flame tube of the burner, the solid obtained is separated from the gas mixture and optionally purified, wherein
  - the oxygen content of the gas containing free oxygen is adjusted such that the lambda value is greater than or equal to 1, and
  - the gamma value is between 1.2 and 1.8.
6. Process according to claim 5, characterised in that silicon halides, organochlorosilicon compounds or organosilicon compounds and mixtures of the above compounds are used as the silicon compound.
7. Use of the silica powder according to claims 1 to 4 for toner applications, in the silicone and rubber industry,

to adjust the rheology of liquid systems, for the production of dispersions, as a filler, for the film-coating of polyethylene terephthalate and polyvinyl acetate, in lacquers and paints.

**Abstract****Pyrogenically produced silica powder**

5 Pyrogenically produced silica powder with a BET surface of 30 to 90 m<sup>2</sup>/g, a dibutyl phthalate number of at least 80 and a tamped density of no more than 110 g/l. It is produced in that at least one vaporous silicon compound,  
10 a gas containing free oxygen and a combustible gas are mixed together in a closed burner and then burnt in a flame in the flame tube of the burner, the solid obtained is separated from the gas mixture and optionally purified, wherein the oxygen content of the gas containing free oxygen is adjusted such that the lambda value is greater than or equal to 1, and the gamma value  
15 is between 1.2 and 1.8. It can be used in toner applications.

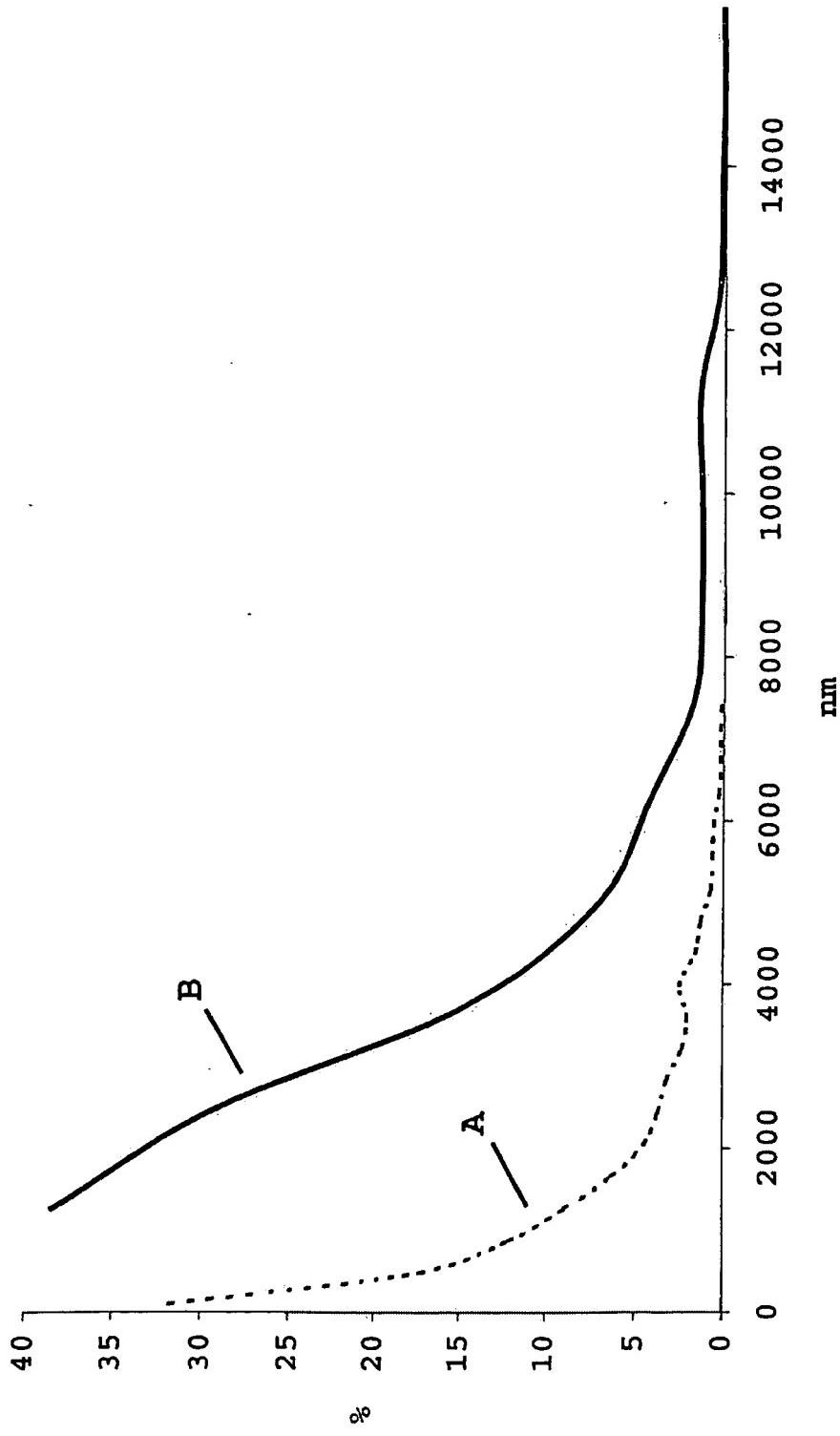


Figure 1